



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

IX.

Examination of Naphtha obtained from Rangoon Petroleum.

BY C. M. WARREN AND F. H. STORER.

Communicated August 9, 1865.

SEVERAL years since, Warren De La Rue and Hugo Müller¹ attempted to determine the chemical composition of the petroleum from Rangoon. But the results obtained by these distinguished chemists were exceedingly unsatisfactory.

De La Rue and Müller operated upon the large scale, having started with a stock of several tons of the crude petroleum; but in so far as concerns the hydro-carbons, which, as they admit, constitute the chief part of the naphtha, these observers confess their inability to separate the mixture into compounds of fixed boiling points.

So soon as the method of separating volatile hydro-carbons by fractional condensation had been successfully employed by one of us,² the desire naturally arose to apply this method to the elucidation of problems which the best chemists of the day had failed to solve. The labors of De La Rue and Müller at once occurred to us as furnishing an extreme instance, and it was determined to test the new process with materials which, as these chemists had shown, could not be unravelled by the old processes of analysis. With this view a sample of native Rangoon Petroleum was obtained, in Jan. 1862, from Price's Patent Candle Co., of London, it being well known to chemists that this firm was at that time constantly importing the petroleum in question. The sample received from Price's Co. amounted to "five imperial gallons;" it was contained in a well-secured vessel, and was accompanied by a certificate of the company to the effect that the petroleum was in the condition in which it is imported into England, — that is, "just as we receive it from Burmah."

The package containing this sample remained in our possession unopened until the autumn of 1863, when the investigation now to be described was commenced. Upon examination the petroleum was found to be a thick, greasy matter, not sufficiently

¹ Proceedings of the Royal Society of London, VIII. 221; or Phil. Mag. 1857, [4.] XIII. 512.

² Warren, Memoirs of American Academy, [N. S.] IX. 121.

liquid to admit of being poured from the can which contained it, when the temperature of the air was $25^{\circ}\text{C}.$; but, upon being heated, it flowed readily at 30° – 33° , and became perfectly fluid at 38° – 40° . The color of the mass was yellowish-green. It emitted the odor common to the purer varieties of native petroleum; though its odor was but slight and in no wise offensive. The specific gravity of this native petroleum was 0.875 at 29° .

Four separate portions of the crude petroleum, each about 5600 *c. c.*, were distilled in a common copper retort without the interposition of any hot condenser. A few drops of the liquid began to distil over at about 140° – 150° , and the process of distillation was continued until the temperature had reached 270° – 300° . The distillate obtained amounted, all told, to a little more than 7000 *c. c.*, or 30.46% of the crude petroleum.

The volatile product, or *naphtha*, thus obtained was now subjected to the process of distillation and fractional condensation, as described in Vol. IX., p. 130, of the Memoirs of this Academy. This *naphtha* began to pass through the hot condenser at about 125° , the liquid in the retort then boiling at about 165° . During a dozen or more operations the distillation was carried up to 260° ; afterwards, as the quantities became smaller, only up to about 250° . The *naphtha* contained only a very small quantity of easily volatile products, nothing having been collected, in a second cold receiver surrounded with ice, either during the preliminary distillation from the copper retort or during the first series of fractional distillations.

Fractions of the *naphtha* were taken off for every ten degrees of temperature at first, then for every five degrees, then for every two degrees, and, finally, for each single degree,—by far the larger part of the work having, of course, been done in fractions of one degree. The greatest care was constantly exercised in order to lessen as far as possible the loss by evaporation of the more volatile products. It is, however, impossible to avoid a great waste of these matters. With the same regard to economy of liquid, the size of the glass retorts and of the worms employed was reduced to the lowest practicable limit.

After the distillatory process had been continued until products of definite boiling points had been obtained, or until, in the lack of this, the amount of liquid in each fraction had been so far reduced that there was no longer any hope of isolating pure substances in that part of the field, a survey of the work indicated that there had been obtained seven well-defined heaps¹ between the temperatures of 170° ² and 250° ; but

¹ For definition of this term see the preceding Memoir, p. 179 of this volume.

² All statements of temperature, when not followed by the word "corrected," refer to the indications of ordinary thermometers. Corrected temperatures are those taken in the manner described in Vol. IX., p. 143 of the Memoirs of this Academy, and corrected for atmospheric pressure, and the upper column of mercury in accordance with H. Kopp's formula.

that below 175° the quantities of liquid had become so small that no definite results could there be obtained. It is true that several elevations existed in this range of small fractions, but to these we will refer hereafter.

It should here be mentioned that we had not been long at work upon this naphtha from Rangoon petroleum, before the conviction was forced upon us that we had started with an insufficient quantity of material. Application was therefore made in the winter of 1863-4 to Price's Patent Candle Company for a supply of the naphtha such as was formerly prepared by them by distilling Rangoon petroleum upon the large scale, but to our regret we learned that the naphtha in question was no longer manufactured by the company, and that it was out of their power to furnish us with any of it. In spite of this, and in fact while the negotiation was pending, we continued to work upon our naphtha as before, being animated by a determination to learn how much could be done with the process of fractional condensation when this is applied to so small a quantity of volatile material as that at our disposal.

Each of the isolated heaps of liquid was now worked by itself, over sodium, until this metal was no longer acted upon, after which the most prominent fractions were analyzed and otherwise examined, as is stated below. It should be noted that neither the crude petroleum, nor the naphtha, nor the finished heaps were ever subjected to the action of any chemicals other than this distillation from sodium which has just been alluded to.

Rutylene = $C_{20}H_{20}$. The heap at 170° - 176° amounted to about 120 c. c. Its summit was very clearly defined at 172° - 173° , this fraction being twice as large as those at 171° - 172° or 174° - 176° , and half as large again as that at 173° - 174° .

The fraction 172° - 173° boiled at 175.8° (corrected).

On analysis, 0.2036 grm. of it gave 0.255 grm. water, and 0.6421 grm. of carbonic acid. Or,

	Found.	Theory.
Carbon,	86.00	C_{20} 85.7
Hydrogen,	13.75	H_{20} 14.3
	<hr/> 99.75	<hr/> 100.00

Determination of vapor density:—

Temperature of balance,	12.5°
“ oil-bath,	223°
Excess of weight of balloon,	0.5745
Capacity “	242 c. c.
Air remaining in “	0 “
Density of vapor found,	5.086
“ “ theoretical ($C_{20}H_{20}$),	4.841

Its specific gravity was found to be 0.823 at 0°.

Heap at 187° = C_n H_n. Immediately above the rutylene heap there was noticed a well-defined tendency toward persistency at 180°–184°, and upon finally working these fractions by themselves, it was found to be impossible to reduce them below a certain size, little or nothing coming off at 180°, and there being no residue worth mentioning at 185°. The summit of this spurious (?) heap remained constant at 182°–184°.

The fraction 182°–183° boiled at 187.4° (corrected).

On analysis, 0.234 grm. of it gave 0.289 grm. of water, and 0.736 grm. of carbonic acid. Or,

	Found.		Theory.
Carbon,	85.77	C _n	85.7
Hydrogen,	13.68	H _n	14.3
	<hr/> 99.45		<hr/> 100.0

Its specific gravity was found to be 0.8356 at 0°.

Margarylene = C₂₂ H₂₂. Between 186° and 193° was a heap amounting to about 215 c. c. the summit of which stood out boldly at 188°–190°.

The fraction 189°–190°, which, by the way, was of precisely the same size of the 188°–189°, boiled at 195.9° (corrected).

On analysis, 0.1407 grm. of it gave 0.175 grm. water, and 0.4469 grm. carbonic acid. Or,

	Found.		Theory.
Carbon,	86.64	C ₂₂	85.7
Hydrogen,	13.79	H ₂₂	14.3
	<hr/> 100.43		<hr/> 100.0

A determination of vapor density resulted as follows:—

Temperature of balance,	13.5°
“ oil-bath,	249°
Excess of weight of balloon,	0.5697
Capacity	“	231 c. c.
Air remaining in	“	0
Height of barometer,	759mm. at — 2°
Density of vapor found,	5.478
“ “ “ theoretical (C ₂₂ H ₂₂),	5.325

Its specific gravity was found to be 0.8398 at 0°.

Laurylene = C₂₄ H₂₄. Between 200° and 214° there were three distinct summits amounting respectively to about 125 c. c., 150 c. c., and 150 c. c. These summits were well defined, particularly the lower one, the true boiling point of which was found to be 208.3° (corrected); the second summit boiled at 214.6° (corrected), and the third at 219.5° (corrected).

On analysis, the following results were obtained; No. I. refers to the fraction which boiled at 208.3° (corrected); No. II. to that boiling at 214.6° ; and No. III. to that boiling at 219.5° . 0.1845 grm. of No. I. gave 0.2121 grm. water, and 0.5885 grm. carbonic acid (*a*); a second sample of 0.1326 grm. of No. I. gave 0.1525 grm. water, and 0.4235 grm. carbonic acid (*b*); 0.1387 grm. of No. II. gave 0.1654 grm. water, and 0.443 grm. carbonic acid (*a*); a second sample, of 0.1433 grm., of No. II. gave 0.1728 grm. water, and 0.4552 grm. carbonic acid (*b*); while 0.194 grm. of No. III. gave 0.2407 grm. water, and 0.6106 grm. carbonic acid. Or,

	I.		Found. II.		III.	Theory. ($C_{24}H_{24}$)
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>		
Carbon,	86.99	87.10	87.09	86.60	85.83	85.7
Hydrogen,	12.79	12.82	13.27	13.40	13.87	14.3
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	99.78	99.92	100.36	100.00	99.70	100.0

These figures accord with the formulæ I. (*a*) $C_{24}H_{21.19}$, (*b*) $C_{24}H_{21.20}$; — II. (*a*) $C_{24}H_{21.95}$, (*b*) $C_{24}H_{22.29}$; — III. $C_{24}H_{23.28}$; and point clearly to the presence of some substance less highly hydrogenized than laurylene. In a subsequent paragraph it will be shown that this disturbing element was naphthalin. That the naphthalin should have given rise to the formation of three heaps is a matter of no surprise in the present instance, since unfortunately the work of two operators happened to overlap at this very point. One obtained the greater part of the naphthalin, the other most of the laurylene; while between the two a spurious heap¹ was formed.

A determination of the vapor density of Nos. II. and III. gave the following results: —

	II.	III.
Temperature of balance,	12.5°	13°
“ “ oil-bath,	256.5°	262°
Excess of weight of balloon,	0.6247	0.6238
Capacity “	228 c. c.	226.5 c. c.
Air remaining in “	0 “	0 “
Height of barometer,	759mm. at $— 2^{\circ}$	748.6mm. at 3°
Density of vapor found,	5.980	6.051
“ “ theoretical ($C_{24}H_{24}$),	5.809	5.809

The specific gravity of No. I. was found to be 0.8654 at 0° ; that of No. II. to be 0.8548 at 0° ; and that of No. III. to be 0.8453 at 0° .

Naphthalin = $C_{20}H_8$. In the course of the winter it happened that the temperature of the apartment in which the products from the Rangoon naphtha were kept, fell to 1° or 2° below zero, and remained at that point during several days. It was then

¹ See this volume, p. 200.

noticed that an abundant crop of crystalline plates had separated out in the fraction which boiled at 208° (corrected), and the fraction next above, namely, 209° (corrected). The quantity of these crystals was large as compared with the amount of liquid from which they had been deposited. After they had been removed from the liquid, a second crop of crystals was obtained from the same fractions, by cooling them in a mixture of ice and salt. These crystals were specially abundant, as before, in the fraction 208° (corrected); but no crystals were obtained, by the treatment with ice and salt, from any of the neighboring fractions, or from any of the fractions in the heap at 214.6° (corrected). Nor were any crystals deposited during the continuance of the cold weather from any of the other products which we have obtained from the Rangoon naphtha. The crystals from fractions 208° , 209° (corrected), were allowed to drain and were then pressed gently between folds of filter paper so long as any oil could be thus removed from them. During these operations the crystals remained unchanged; excepting in so far as they developed the unmistakable odor of naphthalin. Like those of pure naphthalin from coal-tar, the crystals were not very soluble in cold spirit, but on warming the spirit they dissolved in the same manner as crystals of pure naphthalin. In cold ether they dissolved in the same way as the crystals of naphthalin, and crystallized out again like naphthalin; a portion of the crystals in each case, that is, both the crystals from Rangoon naphtha and those from coal-tar, sublimed into the upper part of the test-tube in which the solution was effected, and were deposited there in the well-known characteristic plates. The crystals from fraction 208° (corrected) melted at 74° . A portion of them having been maintained during some time at a temperature slightly superior to 90° , a sublimate of the characteristic plates already alluded to was deposited upon the cold upper part of the tube above the source of heat.

On analysis, 0.167 grm. of the crystals first deposited from fraction 208° (corrected) gave 0.1015 grm. water and 0.5729 grm. carbonic acid. Or,

	Found.		Theory.
Carbon,	93.53	C ₂₀	93.75
Hydrogen,	6.70	H ₈	6.25
	100.23		100.00

Cocinyene = C₂₆ H₂₆. The last heap in our series was at 226° – 234° , the summit of it being at 229° – 232° , each of the fractions 229° – 230° , 230° – 231° , and 231° – 232° being very nearly of equal size, though each was considerably larger than any others in the heap. The fraction 230° – 231° was a trifle larger than the others. The quantity of liquid in the whole heap 226° – 234° amounted to about 325 c. c. Above 234°

the quantities of liquid in the degree-fractions fell away to almost nothing; there is evidently no compound present between 234° and 250° .

The fraction 230° – 231° boiled at 232.75° (corrected).

On analysis, 0.2871 grm. of the fraction 230° – 231° gave 0.3541 grm. water, and 0.91 grm. carbonic acid. Or,

	Found.	Theory.
Carbon,	86.38	C ₂₆ 85.7
Hydrogen,	13.69	H ₂₆ 14.3
	<hr/> 100.07	<hr/> 100.0

In determining the vapor-density of this substance the balloon was filled with an atmosphere of carbonic acid¹ after the introduction of the liquid. The following result was obtained:—

Temperature of balance,	22°
“ “ oil-bath,	274°
Excess of weight of balloon,	0.6863
Capacity “	233 c. c.
Air remaining in “	0
Height of barometer,	760.5 m. m. at 21°
Density of vapor found,	6.4225
“ “ theoretical (C ₂₆ H ₂₆),	6.2940

The specific gravity of the fraction 230° – 231° was found to be 0.8445 at 0° .

The attempts which we have made to isolate the constituents of that portion of Rangoon naphtha which is more volatile than the hydro-carbons above described, were unsuccessful; the quantity of naphtha boiling at temperatures lower than 175° having been so small that it could not be thoroughly analyzed by the process of fractional condensation. After protracted efforts to separate these volatile hydro-carbons from one another by means of a diminutive apparatus, we were at last reluctantly forced to abandon the attempt, and to acknowledge our inability to obtain satisfactory results from such small quantities of the complex material.

Indeed, the quantity of volatile naphtha at our disposal was so small that although at the last it was divided only into fractions of wide range, each of them representing three or more degrees of temperature, these portions in several instances soon became too minute to be operated upon at all, even in the smallest practicable apparatus. But since these volatile products had been subjected, first and last, to a large number of distillations and fractional condensations, each of the fractions finally obtained must have

¹ In a previous attempt to determine this vapor-density in the usual way, without employing carbonic acid, the mixture of air and vapor in the balloon took fire with a slight explosion, the temperature of the oil-bath being then at 321° .

been tolerably well purified from all substances, excepting those whose boiling points are not widely different from its own. We have, therefore, taken pains to analyze some of the more prominent among the fractions into which the volatile portion of the naphtha had been divided, in order to learn whether there might not thus be obtained a general idea of the composition of this part of the naphtha.

The following is a record of the analyses in question, — all statements of degrees of temperature here referring to “corrected” boiling points: —

I. One portion (*a*) of the fraction 98°–109°, this being the most volatile¹ of all the products which we have obtained from Rangoon petroleum, gave 0.3294 grm. water and 0.771 grm. carbonic acid; another portion (*b*) gave 0.4533 grm. water and 1.0673 grm. carbonic acid.

II. 0.194 grm. of the fraction 121.6°–123.5° gave 0.2589 grm. water and 0.6022 grm. carbonic acid.

III. 0.2987 grm. of the fraction 142.3°–144.3° gave 0.3799 grm. water and 0.9416 grm. carbonic acid.

IV. 0.1583 grm. of the fraction 151.6°–153.7° gave 0.2048 grm. water and 0.4952 grm. carbonic acid; another portion (*b*) gave 0.1346 grm. water and 0.3245 grm. carbonic acid.

V. A portion of the fraction 154.7°–155.7° gave 0.2002 grm. water and 0.491 grm. carbonic acid.

VI. 0.1554 grm. of the fraction 158.8°–159.8° gave 0.1986 grm. water and 0.488 grm. carbonic acid.

VII. 0.1714 grm. of the fraction 164°–165° gave 0.2174 grm. water and 0.5422 grm. carbonic acid.

VIII. 0.1899 grm. of the fraction 172.3°–173.8° gave 0.2398 grm. water and 0.5992 grm. carbonic acid.

Reducing these results to per cents., we have

	I.		II.	III.	IV.	
	<i>a</i>	<i>b</i>			<i>a</i>	<i>b</i>
Carbon,	85.18	85.27	84.64	85.97	85.34	85.59
Hydrogen,	14.82	14.73	14.85	14.13	14.40	14.41
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	99.49	100.10	99.74	100.00
	V.		VI.	VII.	VIII.	
Carbon,	85.79		85.65	86.23	86.04	
Hydrogen,	14.21		14.16	14.06	14.01	
	<hr/>		<hr/>	<hr/>	<hr/>	
	100.00		99.81	100.29	100.05	

¹ It should be remembered, in this connection, that De La Rue and Müller, by operating upon large quantities of the petroleum, obtained products boiling as low as 50°.

From these analyses the following formulæ are derived:—

I. (a) = $C_{14} H_{14.62}$; (b) = $C_{14} H_{14.51}$. II. $C_{16} H_{16.85}$. III. $C_{16} H_{15.78}$. IV. (a) = $C_{18} H_{18.23}$; (b) = $C_{18} H_{18.19}$. V. $C_{18} H_{17.9}$. VI. $C_{18} H_{17.86}$. VII. $C_{18} H_{17.54}$. VIII. $C_{18} H_{17.59}$.

It will be observed that the fractions Nos. I. and II. are largely composed of hydrides, — doubtless those of œnanthyl and of capryl, which boil at 98°, 120°, and 128°, — though still contaminated with hydro-carbons belonging to one or both of the $C_n H_n$ series, or possibly even with toluole. Fraction No. III. is probably a mixture of xylol, the foregoing hydrides, and members of the $C_n H_n$ series, as before. The composition of fraction No. IV. indicates the probable presence of hydride of pelargonyl, boiling at 150°. Fractions Nos. V., VI., VII., and VIII. are probably composed for the most part of pelargonene ($C_{18} H_{18}$) contaminated with a little isocumole ($C_{18} H_{12}$).

The comparatively small proportion of hydrogen found in the fractions which boil in the vicinity of 140° and 170° (the boiling points of xylol and isocumole), goes to corroborate the opinion of De La Rue and Müller,¹ that Rangoon petroleum contains members of the benzole series, and is perhaps all the more pertinent in view of the fact that we have ourselves isolated naphthalin from the petroleum, as has been already stated. It is of course conceivable that the naphthalin alone may have contaminated the fractions in question, as well as the definite heaps which have been previously described, the analysis of all of which indicate the presence of a little less hydrogen than is contained in pure $C_n H_n$. But this conception seems to us improbable; the composition of fractions 142.3°–144.3° (No. III.) and 151.6°–153.7° (No. IV.), in particular, would appear to invalidate it. We may here say that on the whole our results have very much weakened the opinion, which at one time seemed to us to be not altogether improbable, that the benzole-homologues obtained by De La Rue and Müller might have resulted from the action of nitric acid in removing hydrogen from the more highly hydrogenized hydro-carbons, and might not have been contained in the native petroleum.

As the result of our examination thus far, it appears that the naphtha from Rangoon petroleum contains:—

Rutylene = $C_{20} H_{20}$	boiling at about	175°
Margarylene = $C_{22} H_{22}$	“ “ “	195°
Laurylene = $C_{24} H_{24}$	“ “ “	215°
Cocinylene = $C_{26} H_{24}$	“ “ “	235°
Naphthalin = $C_{20} H_8$.		

Also, probably, Pelargone = $C_{18} H_{18}$, boiling at about 155°, and members of one or both of the series of hydrides; it being a fair presumption that we have had in our hands the Hydrides of œnanthyl, of Capryl, and of Pelargonyl. Our experiments also indicate the probable presence of Xylol and Isocumole.

¹ Proceedings of the Royal Society of London, VIII. 225.